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Chemosensors containing appended benzothiazole group(s): Selective binding of Cu²⁺ and Zn²⁺ Ions by two related receptors

Deepak Bansal[a] and Rajeev Gupta[*a]

Amide-benzothiazole based receptors act as the highly selective chemosensors for Cu(II) and Zn(II) ions both in solution and in the solid states. Binding and crystallographic studies have been used to shed light on the mechanism of interaction between chemosensors and metal ions.

Copper and zinc ions play important role in different biological processes.[1] Balanced concentration of copper ion is required for smooth functioning of liver and kidney whereas accumulation leads to adverse effect on gastrointestinal process in addition to damage to liver and kidney.[2] Zinc ion is known to perform assorted physiological and enzymatic functions in living organisms. Imbalance of zinc leads to various diseases such as Alzheimer's, Parkinson's, Menkes and Wilson's diseases.[3] Therefore, design and development of chemosensors for assorted metal ions[4] particularly for copper[5] and zinc[6] ions has been a significant area of research. Out of various sensors, fluorescent chemosensors tender better advantages in terms of fast response time and low analyte concentration thus enabling to perform real time monitoring especially under the biological conditions.[7] Herein, we report two amide-benzothiazole based receptors for the selective detection of Cu(II) and Zn(II) ions.

Receptors **1**-**4** were developed for the potential sensing applications (Fig. S1-S3, ESI).[8] Notably, while receptors **1–3** offer a pincer cavity based on pyridine-2,6-dicarboxamide scaffold; **4** is a half synthetic analogue of **1**. Further, while receptors **1** and **2** symmetrically provide either benzothiazole or benzimidazole groups; **3** has a combination of benzothiazole and *para*-anisidine rings. Chemosensor **1**, exhibits strong emission at 470 nm when excited at 310 nm, was tested towards a large number of metal ions. Importantly, chemosensor **1** was noted to have preferential binding affinity

for the Cu(II) ion out of Na⁺, Mg²⁺, K⁺, Ca²⁺, Sc³⁺, Cr³⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Hg²⁺ ions (Fig. 1a).
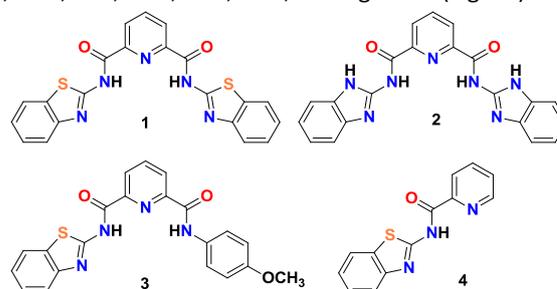
Scheme 1. Chemical drawings of chemosensors used and discussed in this work.

To evaluate the role of cavity and appended heterocyclic rings; receptors **2** (containing appended benzimidazole rings); **3** (one of the appended benzothiazole ring being replaced with *para*-anisidine unit); and **4** (half synthetic analogue of **1**) were tested (Fig. S4 and S5, ESI). Notably, receptors **2**-**4** were found to bind with almost every metal ion; therefore, not exhibiting any selectivity. Thus, it can be concluded that the presence of a pincer cavity as well as two appended benzothiazole rings is an essential requirement for the selective sensing of Cu(II) ion.[9] It is noteworthy that the selectivity of **1** is independent of the choice of copper salts employed; giving nearly identical results with Cl⁻, OAc⁻, ClO₄⁻, and SO₄²⁻ anions (Fig. S6, ESI).

Interestingly, although chemosensor **4** was not selective towards Cu(II) ion, depicting the importance of a pincer cavity, showed exceptionally high selectivity for the Zn(II) ion. Thus, when chemosensor **4** was treated with various metal ions (e.g., Na⁺, Mg²⁺, K⁺, Ca²⁺, Sc³⁺, Cr³⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, and Hg²⁺ ions), either no considerable change or minor decrease in the emission intensity was observed. However, addition of Zn(II) ion resulted in an immediate three-fold enhancement in the fluorescence intensity (Fig. 2a).[10,11] It is important to note that receptors **1 – 3** do not show any binding affinity for the Zn(II) ion suggesting the uniqueness of chemosensor **4**.

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Fig. 1 (a) Change in emission intensity of **1** after the addition of different metal ions (5 equiv.); Inset: relative change in emission intensity of **1** on the addition of different metal ions. (b) Change in emission intensity of **1** (0.1mM) with increasing concentration of Cu(II) ion (0-0.2 mM); (Inset, top): mole ratio plot of **1** with Cu(II) ion; (Inset, bottom): linear regression fitting for 1:1 binding of **1** with Cu(II) ion. All studies are in THF.

Fig. 2 (a) Change in emission intensity of **4** after the addition of different metal ions (5 equiv.); Inset: relative change in emission intensity of **4** on the addition of different metal ions. (b) Change in emission intensity of **4** (0.1mM) with increasing concentration of Zn(II) ion (0-0.2 mM); (Inset, top): Job's plot of **4** with Zn(II) ion; (Inset, bottom): linear regression fitting for 1:1 binding of **4** with Zn(II) ion. All studies are in THF.

Subsequently, concentration dependent absorption and emission spectral titrations of chemosensors **1** and **4** with Cu(II) and Zn(II) ions were performed. In case of **1**, a gradual quenching of emission intensity was observed as a function of Cu(II) ion concentration while complete quenching was noted after the addition of 1 equiv. (Fig. 1b). For **4**, an increase in the emission intensity was noted with maximum intensity reaching at ca. 1 equiv. of Zn(II) ion (Fig. 2b). In both cases, mole ratio plot and linear regression as well as least-square fitting[12] substantiate a 1:1 stoichiometry between the chemosensors **1** and **4** with Cu(II) and Zn(II) ions, respectively (Fig. S7 and S8, ESI).

The absorption spectral titration exhibited two well-defined isosbestic points at 280 and 325 nm during the titration between **1** and Cu(II) ion (Fig. S7-9, ESI) whereas a similar titration of **4** with Zn(II) ion displays isosbestic points at

270 and 320 nm (Fig. S9-S14, ESI). The observation of well-anchored isosbestic points clearly suggests clean transformation of one species to another. Such absorption spectral titrations further established a 1:1 stoichiometry for chemosensors **1** and **4** towards the respective metal ion. The binding coefficients and association coefficients, calculated using the Benesi–Hildebrand equation,[13] show that the measured emission or absorption intensity, $1/[I-I_o]$, both for **1** and **4**, varied in a linear relationship as a function of $1/[M^{2+}]$. This further confirms a 1:1 stoichiometry between chemosensors **1** and **4** to that of Cu(II) or Zn(II) ion, respectively. Binding constants using fluorescence titrations were 3.1×10^6 and 3.0×10^6 (M^{-1}) for **1** and **4**, respectively.[13] Such numbers were further supported when calculated from the absorption spectral titrations following three different wavelengths.[13] Chemosensor **1** with Cu(II) ion provided binding constants ($\times 10^6$ M^{-1}) of 6.8, 7.8, and 5.1 at 260, 310, and 335

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nm, respectively. Similarly, chemosensor **4** with Zn(II) ion afforded binding constants (x 10^6 M^{-1}) of 1.0, 2.1, and 1.6 at 260, 310, and 335 nm, respectively.

We then attempted to understand the binding between chemosensor **1** and Cu(II) ion that led to the isolation of **1**-Cu after treating **1** with [Cu(H$_2$O)$_6$](ClO$_4$)$_2$ in THF.[8] FTIR spectrum of **1**-Cu exhibits hypsochromically shifted NH resonances at 3285 cm^{-1} while $\nu_{C=O}$ and ClO$_4^-$ stretches were noted at 1660 and 1050-1130 cm^{-1}, respectively (Fig. S15, ESI). The high-resolution mass spectrum of **1**-Cu in THF displays the molecular ion peak at 729.1520 with isotope patterns matching the theoretical values corresponding to {[Cu(**1**)(H$_2$O)$_2$](ClO$_4$)$_2$+H$^+$} (Fig. S16, ESI).[14] The microanalysis data further corroborated these findings. Collectively, these studies suggest that the ligand coordinates the Cu(II) ion in its dianionic form while the amidic protons have been re-located to the appended benzothiazole rings. Such a movement of proton(s) is quite interesting; however, has been observed by us[13c] and others[15] with similar amide-based pincer cavities.
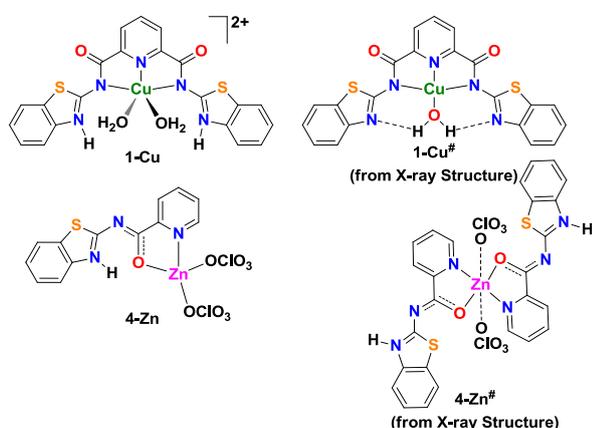
Scheme 2. Chemical drawings of Cu(II) and Zn(II) complexes synthesized and discussed in this work.

Interestingly, when **1**-Cu was recrystallized from DMF; a new compound with the following composition was obtained: [Cu(**1**-2H$^+$)(H$_2$O)] (**1**-Cu$^\#$).[8] **1**-Cu$^\#$ was crystallographically characterized to display a four-coordinated planar geometry around the Cu(II) ion wherein metal is bound to the N$_3$ pincer cavity while additionally ligated by a water molecule (Fig. 3).[16] The coordinated water molecule forms *intramolecular* H-bonds with the appended benzothiazole groups. The crystal structure of **1**-Cu$^\#$ shows the coordination of Cu(II) ion by the dianionic ligand while absence of perchlorate ions as noted in **1**-Cu. Such structural features suggest possible removal of perchlorate ions (ClO$_4^-$) in the form of HClO$_4$ during the recrystallization of **1**-Cu from DMF. Therefore, p*H* was measured during the dissolution of **1**-Cu in DMF. Notably, p*H* of a 1 mM solution of chemosensor **1** was found to be ca. 8.5 whereas p*H* of **1**-Cu was observed to be ca. 4.2 suggesting the release of perchloric acid while dissolving this compound in DMF. For reference, p*H* of **1**-Cu$^\#$ in DMF was found to be ca. 8.4, quite similar to that of chemosensor **1**. Additional evidences for the proton movement came from the conductivity measurements.[17] Such an experiment showed 1:2

electrolytic nature of **1**-Cu in DMF whereas **1**-Cu$^\#$ exhibited no considerable conductance suggesting a neutral composition. It is important to note that while recording the mass spectrum of **1**-Cu either in MeOH or MeCN (Fig. S17, ESI); the molecular ion peak corresponds to **1**-Cu$^\#$ (Obsd. *m/z*: 528.9484; Calc. 529.0040 for **1**-Cu$^\#$+H$_2$O+H$^+$) and not **1**-Cu. Such a fact suggests higher thermodynamic stability of **1**-Cu$^\#$ over **1**-Cu that led to its crystallization.
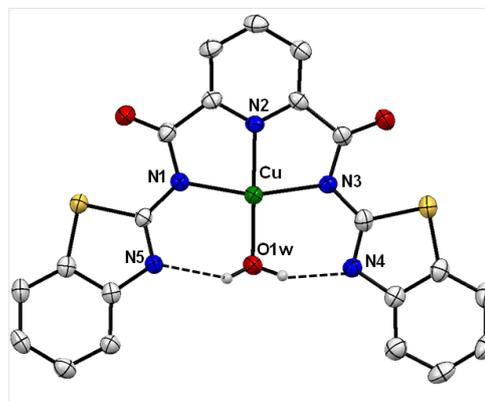
Fig. 3 Crystal structure of **1**-Cu$^\#$; thermal ellipsoids are drawn at 30% level whereas all hydrogen atoms except water molecule are omitted for clarity. Selected bond distances (Å): Cu-N2, 2.013(3); Cu-N3, 1.914(3); Cu-N4, 2.018(3); Cu-O1w, 1.904(2). Selected bond angles (°): O1w-Cu-N3, 176.46(12); N2-Cu-N4, 161.64(10).

We next attempted a similar synthetic exercise for chemosensor **4** with Zn(II) ion.[8] Complex **4**-Zn was obtained as a white solid after treating **4** with [Zn(H$_2$O)$_6$](ClO$_4$)$_2$ in THF.[8] The microanalysis data; and FTIR, ^{1}H NMR, and mass spectra led to the following composition: [Zn(**4**)(ClO$_4$)$_2$] (Fig. S18-20, ESI). Interestingly, when **4**-Zn was recrystallized from MeOH; a bis-chelated complex (**4**-Zn$^\#$) was isolated and structurally characterized (Fig. S21, ESI). The crystal structure displays that the Zn(II) ion is coordinated by two bidentate ligands in their anionic form whereas the protons have been re-located to the appended benzothiazole rings. As a result; both coordinated ligands remain neutral and the +2 charge is balanced by two ClO$_4^-$ ions which additionally bind the Zn(II) ion. Therefore, Zn(II) ion exhibits an octahedral geometry in a N$_2$O$_4$ coordination environment.[†] The protonated benzothiazolium rings form H-bonds with the ClO$_4^-$ ions. The structural identification of **4**-Zn$^\#$ exhibits a 1:2 metal to chemosensor stoichiometry whereas **4**-Zn displayed a 1:1 ratio. Notably, emission and absorption spectral titrations either in THF (Fig. 2) or MeOH[18] (Fig. S22, ESI) followed by fitting using the Benesi–Hildebrand equation ascertained a 1:1 stoichiometry of **4** to that of Zn(II) ion. Furthermore, ^{1}H NMR spectral titration in d$_4$-MeOH additionally proves a 1:1 stoichiometry by monitoring two different pyridine-H atoms (Fig. S23, ESI). Collectively, these studies suggest that the transformation of **4**-Zn to **4**-Zn$^\#$ has occurred during the crystallization.

Despite several reports on Cu(II) and Zn(II) ion sensors,[4-6] simple and cost-effective detection still remains a challenge. We tried different approaches along such a direction. To explore the sensing abilities of the present chemosensors in
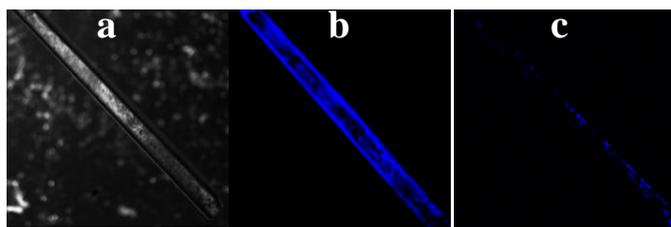
Fig. 4 (a) Bright field microscopic image of a needle shaped crystal of **1**. (b) Fluorescent image of the same crystal under 310 nm UV-light. (c) Quenching in the emission intensity of the same crystal after treating with 1 mM Cu(II) ion solution in water for 10 min.

the solid state; needle-shaped single crystals of **1** and **4** were exposed to 1 mM aqueous solutions of Cu(II) and Zn(II) ions, respectively. As can be seen from Fig. 4; a florescent active crystal of **1** exhibits blue emission after being excited at 310 nm. Notably, when this crystal was exposed to an aqueous solution of Cu(II) ion; the emission intensity was substantially quenched (compare panels b and c). A similar experiment of chemosensor **4** to that of aqueous solution of Zn(II) ion provided the comparable results (Fig. 24, ESI). These experiments depict the chemo-sensing abilities of solid **1** and **4** in aqueous phase.
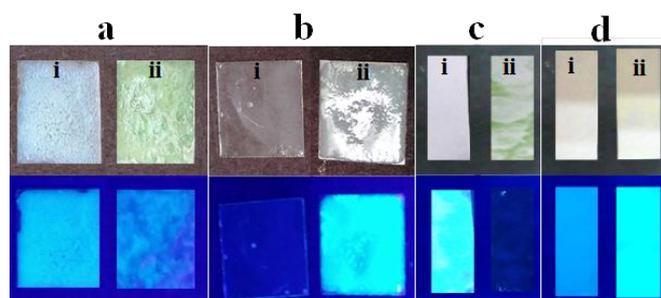
Fig. 5 Polystyrene film on a cover-glass slide containing chemosensor (a) **1** and (b) **4**. Filter paper strips coated with chemosensor (c) **1** and (d) **4**. In all cases, i and ii exhibit images before and after treatment in THF with Cu(II) and Zn(II) ion, respectively whereas 'top' and 'bottom' images signifies daylight and fluorescent images, respectively.

Both **1** and **4** could also be converted into thin peelable films using polystyrene that showed attractive detection abilities for Cu(II) (Fig. 5a) as well as Zn(II) ion (Fig. 5b). To validate a cost-effective detection, filter paper strips[19] were immersed in THF solution of chemosensors **1** and **4** followed by drying in air to prepare test strips. Such test strips were used for the detection by simply dipping them directly into a Cu(II) and Zn(II) ion aqueous solution for a couple of seconds. Detection of Cu(II) ion led to quantitative fluorescence quenching (Fig. 5c) whereas a similar exercise for Zn(II) ion caused florescent enhancement (Fig. 5d). Collectively, these experiments illustrate the potential applications of chemosensors **1** and **4** as the versatile probes for the Cu(II) and Zn(II) ions, respectively. Importantly, both chemosensors **1** and **4** exhibited high detection limits of 2.96×10^{-7} M and 4.71×10^{-8} M, respectively (Fig. S25 and S26, ESI). A comparison to that of literature reports for some of the known chemosensors for copper[5] and zinc[6] ions places **1** and **4** as some of the most effective chemosensors (*cf.* Table S3, ESI).

Reversibility is an important aspect of any receptor to be employed as a chemical sensor for the detection of a specific metal ion. To examine whether the process was reversible for chemosensors **1** and **4**, EDTA was employed.[20] As illustrated in Fig. 6, addition of only one equiv. of Na_2EDTA resulted in nearly quantitative recovery of the florescence of chemosensor **1**. Importantly, reversibility is maintained for several consecutive cycles and exhibits a modular nature of chemosensor **1** in accepting and releasing the Cu(II) ion. A similar experiment using chemosensor **4** also displayed a good reversibility (S27, ESI).
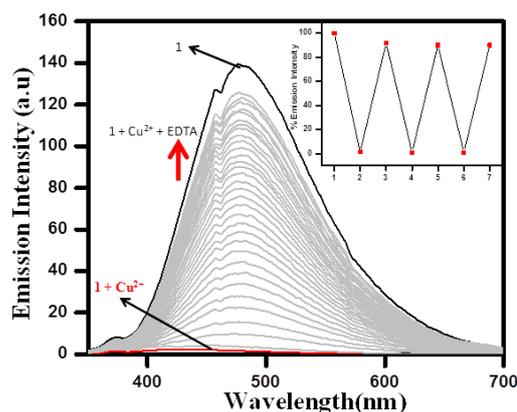
Fig. 6 (a) Recyclability experiment of chemosensor **1** (0.1 mM; black trace); after the addition of one equiv. of Cu(II) ion (red trace); followed by the addition of one equiv. of Na_2EDTA (grey traces). The spectra have been recorded with the intervals of 2 min. The plot exhibits the regeneration of emission intensity of **1** with time. Inset: Four regenerative cycles of chemosensor **1**. The experiment was performed in 9:1 (v/v) $THF-H_2O$ mixture.

Conclusions

This work has shown that simple amide-based receptors containing benzothiazole rings exhibit excellent selectivity towards biologically relevant copper and zinc metal ions. Interestingly, a pincer cavity having two benzothiazole rings made receptor **1** exclusively selective towards Cu(II) ion whereas a single benzothiazole ring in nearly identical design in **4** resulted in a unique selectivity for the Zn(II) ion. Both chemosensors illustrated a high selectivity in solution as well as in the solid state. Of particular interest was the observation of sensing abilities of paper strips in aqueous solutions. Given the remarkable selectivity and sensitivity of chemosensors **1** and **4**; our future studies are directed towards cell imaging and developing solid-state sensing devices.

Acknowledgment

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†The structure solution of **4-Zn#** has resulted in a model in which Zn(II) ion in an asymmetric unit cell receives coordination either from a perchlorate O atom or a water molecule.

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8   See Electronic Supplementary Information (ESI) for the complete synthetic details, Figures, and Tables.

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14 The solid-state diffuse-reflectance absorption spectrum of **1-Cu** displays a broad feature with λ_{max} at ca. 600 nm followed by a low-energy shoulder at ca. 800 nm. Such a spectral feature suggests a square-pyramidal geometry around the Cu(II) ion with $d_{x^2-y^2}$ ground state (Blue trace, Figure S28, ESI). Notably, the five-coordinate geometry is retained when the absorption spectrum is recorded in THF (Black trace, Figure S28, ESI) albeit with red shift. See, B. J. Hathaway in Comprehensive Coordination Chemistry, G. Wilkinson, R. D. Gillard and J. A. McCleverty, ed., Pergamon Press, Oxford, 1987, **5**, 533.

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Graphical Abstract

Chemosensors containing appended benzothiazole group(s): Selective binding of

Cu^{2+} and Zn^{2+} ions by two related receptors

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Artwork:
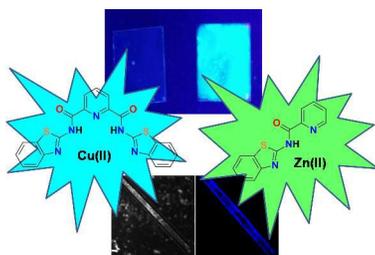
Synopsis: Amide-benzothiazole based molecules act as the highly selective chemosensors for Cu(II) and Zn(II) ions both in solution and in the solid-state.